

The Millimeterwave Spectrum of *n*-Butyl Cyanide

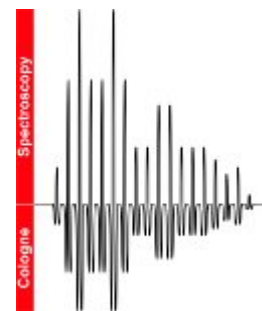
Matthias H. Ordu, University of Cologne

66th OSU International Symposium on Molecular Spectroscopy

22 June 2011 – WF 09



ordu@ph1.uni-koeln.de



Outline

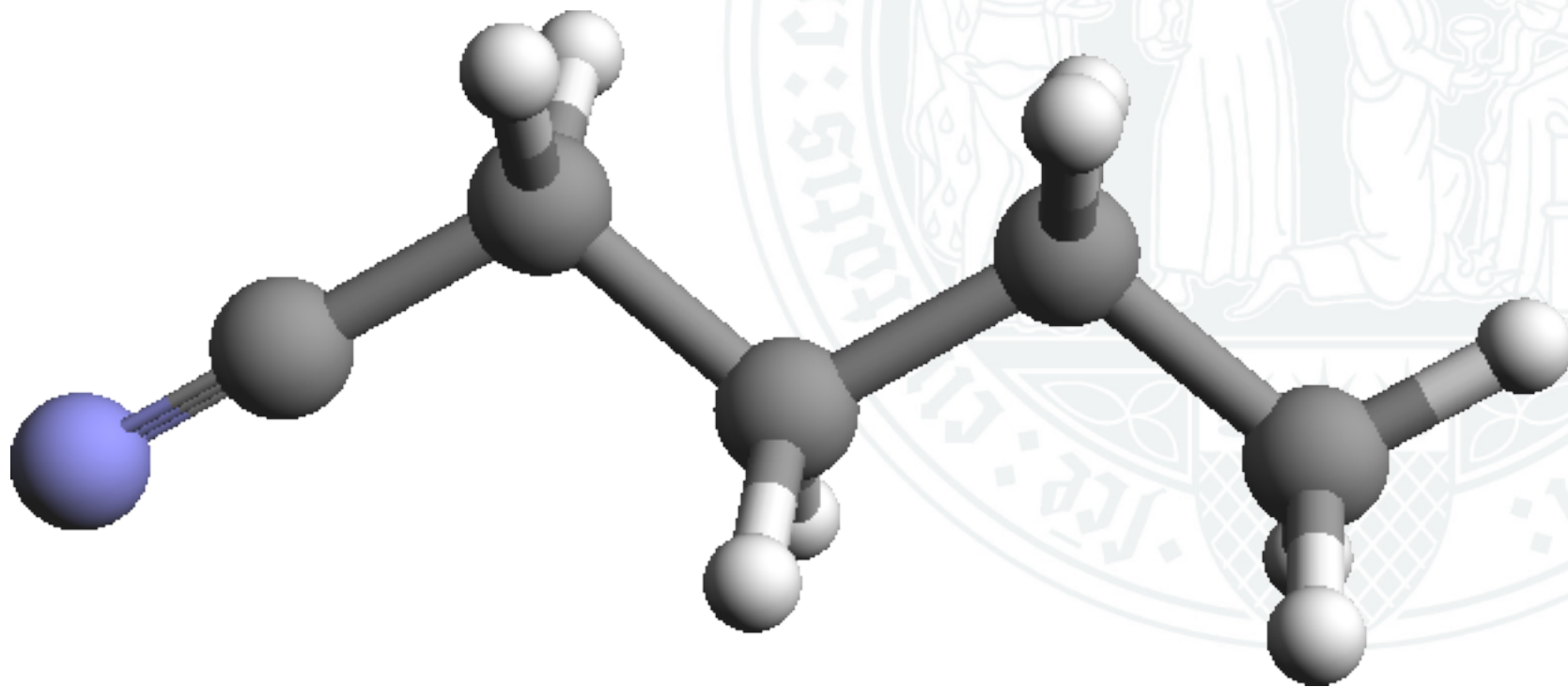
- Why *n*-butyl cyanide?
- The new Cologne MMW spectrometer with 44 m absorption path
- Measurement and analysis of the millimeterwave spectrum
- Conclusion and outlook



Why *n*-Butyl Cyanide?



Structure of *n*-butyl cyanide



Inter- and circumstellar molecules detected so far

2 Atoms	3 Atoms	4 Atoms	5 Atoms	6 Atoms	7 Atoms	8 Atoms	9 Atoms	10 Atoms	11 Atoms	12 Atoms	>12 Atoms
H ₂	C ₃	<i>c</i> -C ₃ H	C ₅	C ₅ H	C ₆ H	CH ₃ C ₃ N	CH ₃ C ₄ H	CH ₃ C ₅ N	HC ₉ N	C ₆ H ₆	HC ₁₁ N
AlF	C ₂ H	<i>l</i> -C ₃ H	C ₄ H	<i>l</i> -H ₂ C ₄	CH ₂ CHCN	HC(O)OCH ₃	CH ₃ CH ₂ CN	(CH ₃) ₂ CO	CH ₃ C ₆ H	C ₂ H ₅ OCH ₃ ?	C ₆₀
AlCl	C ₂ O	C ₃ N	C ₄ Si	C ₂ H ₄	CH ₃ C ₂ H	CH ₃ COOH	(CH ₃) ₂ O	(CH ₂ OH) ₂	C ₂ H ₅ OCHO	<i>n</i> -C ₃ H ₇ CN	C ₇₀
C ₂	C ₂ S	C ₃ O	<i>l</i> -C ₃ H ₂	CH ₃ CN	HC ₅ N	C ₇ H	CH ₃ CH ₂ OH	CH ₃ CH ₂ CHO			
CH	CH ₂	C ₃ S	<i>c</i> -C ₃ H ₂	CH ₃ NC	CH ₃ CHO	H ₂ C ₆	HC ₇ N				
CH ⁺	HCN	C ₂ H ₂	H ₂ CCN	CH ₃ OH	CH ₃ NH ₂	CH ₂ OHCHO	C ₈ H				
CN	HCO	NH ₃	CH ₄	CH ₃ SH	<i>c</i> -C ₂ H ₄ O	<i>l</i> -HC ₆ H	CH ₃ C(O)NH ₂				
CO	HCO ⁺	HCCN	HC ₃ N	HC ₃ NH ⁺	H ₂ CCHOH	CH ₂ CHCHO (?)	C ₈ H ⁻				
CO ⁺	HCS ⁺	HCNH ⁺	HC ₂ NC	HC ₂ CHO	C ₆ H ⁻	CH ₂ CCHCN	C ₃ H ₆				
CP	HOC ⁺	HNCO	HCOOH	NH ₂ CHO		H ₂ NCH ₂ CN					
SiC	H ₂ O	HNCS	H ₂ CNH	C ₅ N						2 Atoms	3 Atoms
HCl	H ₂ S	HOCO ⁺	H ₂ C ₂ O	<i>l</i> -HC ₄ H						SiS	NH ₂
KCl	HNC	H ₂ CO	H ₂ NCN	<i>l</i> -HC ₄ N						CS	H ₃ ⁺
NH	HNO	H ₂ CN	HNC ₃	<i>c</i> -H ₂ C ₃ O						HF	H ₂ D ⁺ , HD ₂ ⁺
NO	MgCN	H ₂ CS	SiH ₄	H ₂ CCNH (?)						HD	SiCN
NS	MgNC	H ₃ O ⁺	H ₂ COH ⁺	C ₅ N ⁻						FeO ?	AlNC
NaCl	N ₂ H ⁺	<i>c</i> -SiC ₃	C ₄ H ⁻							O ₂	SiNC
OH	N ₂ O	CH ₃	HC(O)CN							CF ⁺	HCP
PN	NaCN	C ₃ N ⁻								SiH ?	CCP
SO	OCS	PH ₃ ?								PO	AlOH
SO ⁺	SO ₂	HCNO								AlO	H ₂ O ⁺
SiN	<i>c</i> -SiC ₂	HOCN								OH ⁺	H ₂ Cl ⁺
SiO	CO ₂	HSCN								CN ⁻	
										SH ⁺	

Source: CDMS 12 / 2010



Inter- and circumstellar molecules detected so far

2 Atoms	3 Atoms	4 Atoms	5 Atoms	6 Atoms	7 Atoms	8 Atoms	9 Atoms	10 Atoms	11 Atoms	12 Atoms	>12 Atoms
H ₂	C ₃	<i>c</i> -C ₃ H	C ₅	C ₅ H	C ₆ H	CH ₃ C ₃ N	CH ₃ C ₄ H	CH ₃ C ₃ N	HC ₉ N	C ₆ H ₆	HC ₁₁ N
AlF	C ₂ H	<i>l</i> -C ₃ H	C ₄ H	<i>l</i> -H ₂ C ₄	CH ₂ CHCN	HC(O)OCH ₃	CH ₃ CH ₂ CN	(CH ₃) ₂ CO	CH ₃ C ₆ H	C ₂ H ₅ OCH ₃ ?	C ₆₀
AlCl	C ₂ O	C ₃ N	C ₄ Si	C ₂ H ₄	CH ₃ C ₂ H	CH ₃ COOH	(CH ₃) ₂ O	(CH ₂ OH) ₂	C ₂ H ₅ OCHO	<i>n</i> -C ₃ H ₇ CN	C ₇₀
C ₂	C ₂ S	C ₃ O	<i>l</i> -C ₃ H ₂	CH ₃ CN	HC ₅ N	C ₇ H	CH ₃ CH ₂ OH	CH ₃ CH ₂ CHO			
CH	CH ₂	C ₃ S	<i>c</i> -C ₃ H ₂	CH ₃ NC	CH ₃ CHO	H ₂ C ₆	HC ₇ N				
CH ⁺	HCN	C ₂ H ₂	H ₂ CCN	CH ₃ OH	CH ₃ NH ₂	CH ₂ OHCHO	C ₈ H				
CN	HCO	NH ₃	CH ₄	CH ₃ SH	<i>c</i> -C ₂ H ₄ O	<i>l</i> -HC ₆ H	CH ₃ C(O)NH ₂				
CO	HCO ⁺	HCCN	HC ₃ N	HC ₃ NH ⁺	H ₂ CCHOH	CH ₂ CHCHO (?)	C ₈ H ⁻				
CO ⁺	HCS ⁺	HCNH ⁺	HC ₂ NC	HC ₂ CHO	C ₆ H ⁻	CH ₂ CCHCN	C ₃ H ₆				
CP	HOC ⁺	HNCO	HCOOH	NH ₂ CHO		H ₂ NCH ₂ CN					
SiC	H ₂ O	HNCS	H ₂ CNH	C ₅ N						2 Atoms	3 Atoms
HCl	H ₂ S	HOCO ⁺	H ₂ C ₂ O	<i>l</i> -HC ₄ H						SiS	NH ₂
KCl	HNC	H ₂ CO	H ₂ NCN	<i>l</i> -HC ₄ N						CS	H ₃ ⁺
NH	HNO	H ₂ CN	HNC ₃	<i>c</i> -H ₂ C ₃ O						HF	H ₂ D ⁺ , HD ₂ ⁺
NO	MgCN	H ₂ CS	SiH ₄	H ₂ CCNH (?)						HD	SiCN
NS	MgNC	H ₃ O ⁺	H ₂ COH ⁺	C ₅ N ⁻						FeO ?	AlNC
NaCl	N ₂ H ⁺	<i>c</i> -SiC ₃	C ₄ H ⁻							O ₂	SiNC
OH	N ₂ O	CH ₃	HC(O)CN							CF ⁺	HCP
PN	NaCN	C ₃ N ⁻								SiH ?	CCP
SO	OCS	PH ₃ ?								PO	AlOH
SO ⁺	SO ₂	HCNO								AlO	H ₂ O ⁺
SiN	<i>c</i> -SiC ₂	HOCN								OH ⁺	H ₂ Cl ⁺
SiO	CO ₂	HSCN								CN ⁻	
										SH ⁺	

Source: CDMS 12 / 2010



Scientific goals

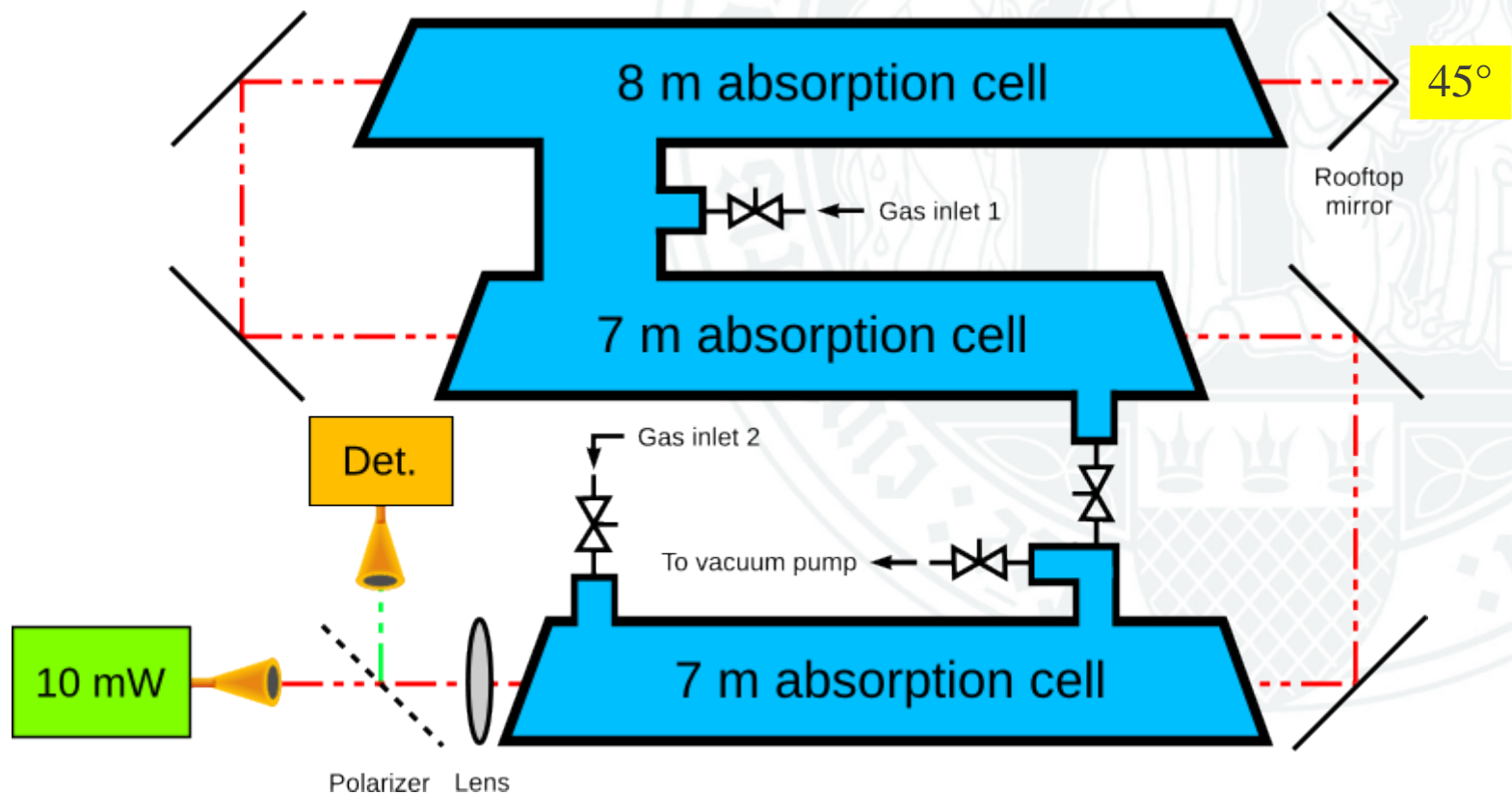
- Detect n-butyl cyanide in space
 - ▶ Measure the rotational spectrum in the lab
 - ▶ Fit the rotational transitions
 - ▶ Predict the spectrum up to ~ 300 GHz
- Extend knowledge about molecular properties
 - ▶ Find experimental evidence for 2 predicted subspecies
 - ▶ Measure the dipole moment



The New Cologne Millimeterwave Spectrometer With 44 m Absorption Path

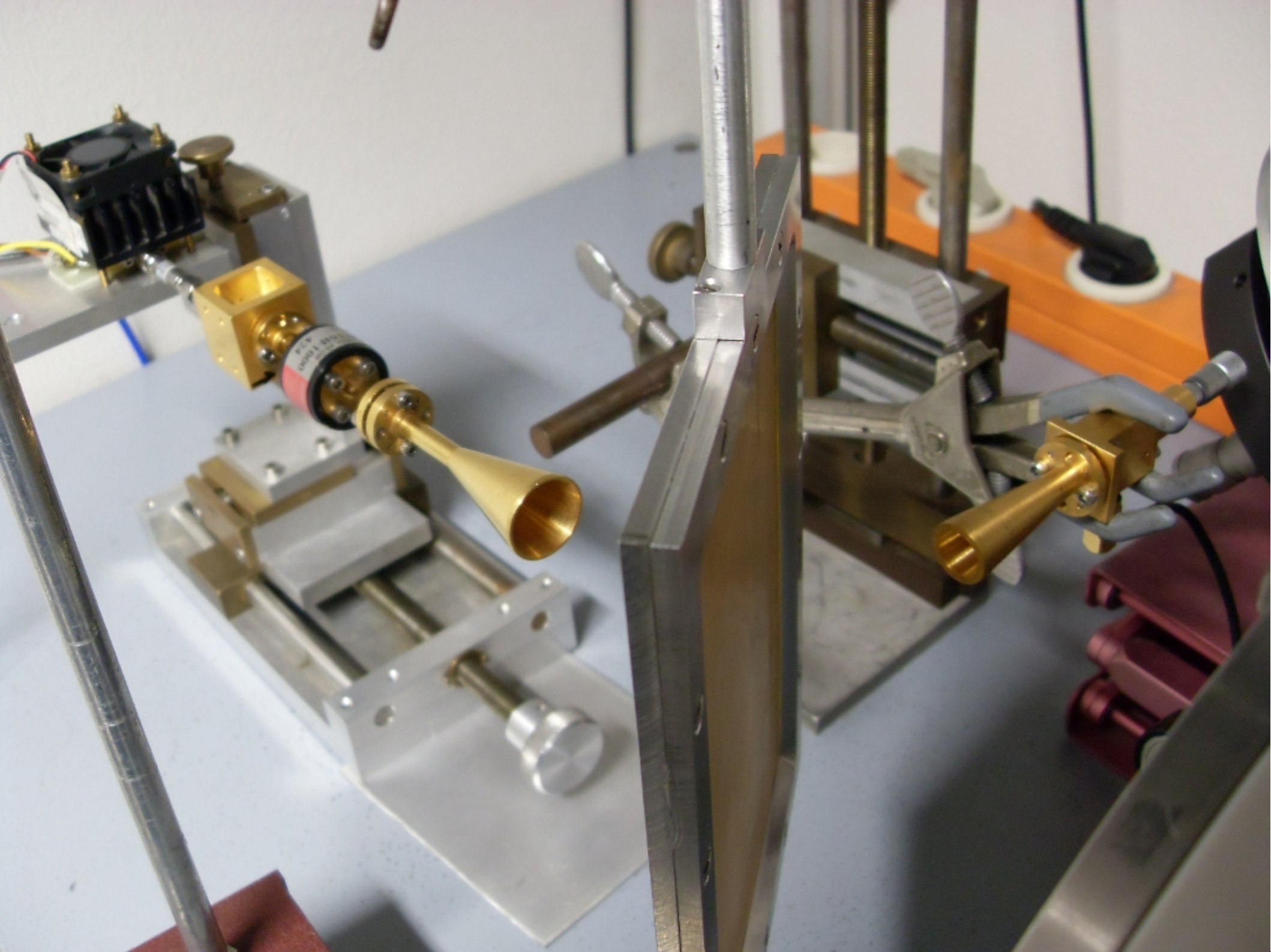


How to get a 3 mm beam twice through a 22 m cell (\varnothing 10 cm) without refocusing









Performance of the spectrometer

- Signal-to-noise ratio determined from ethanol line scans at 3 different cell lengths
 - ▶ 14-fold increased sensitivity compared to a 3 m cell

- Minimum detectable absorption coefficient determined from SNR and catalog intensity:

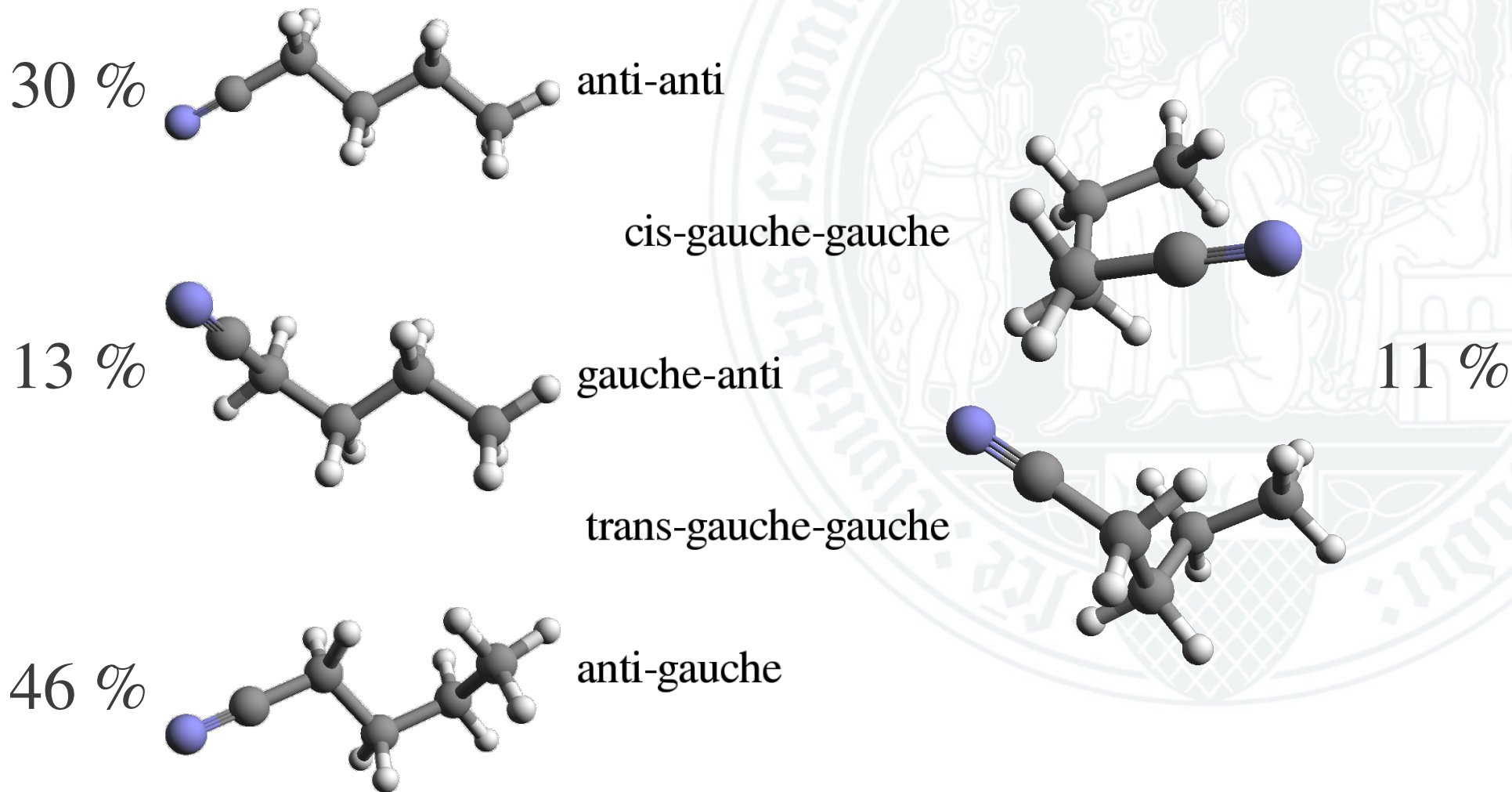
$$\mu_{min} = 2.7 \cdot 10^{-7} \text{ cm}^{-1} \quad \left(I = I_0 e^{-\mu l} \right)$$



Measurement and Analysis of the Millimeterwave Spectrum of *n*-Butyl Cyanide



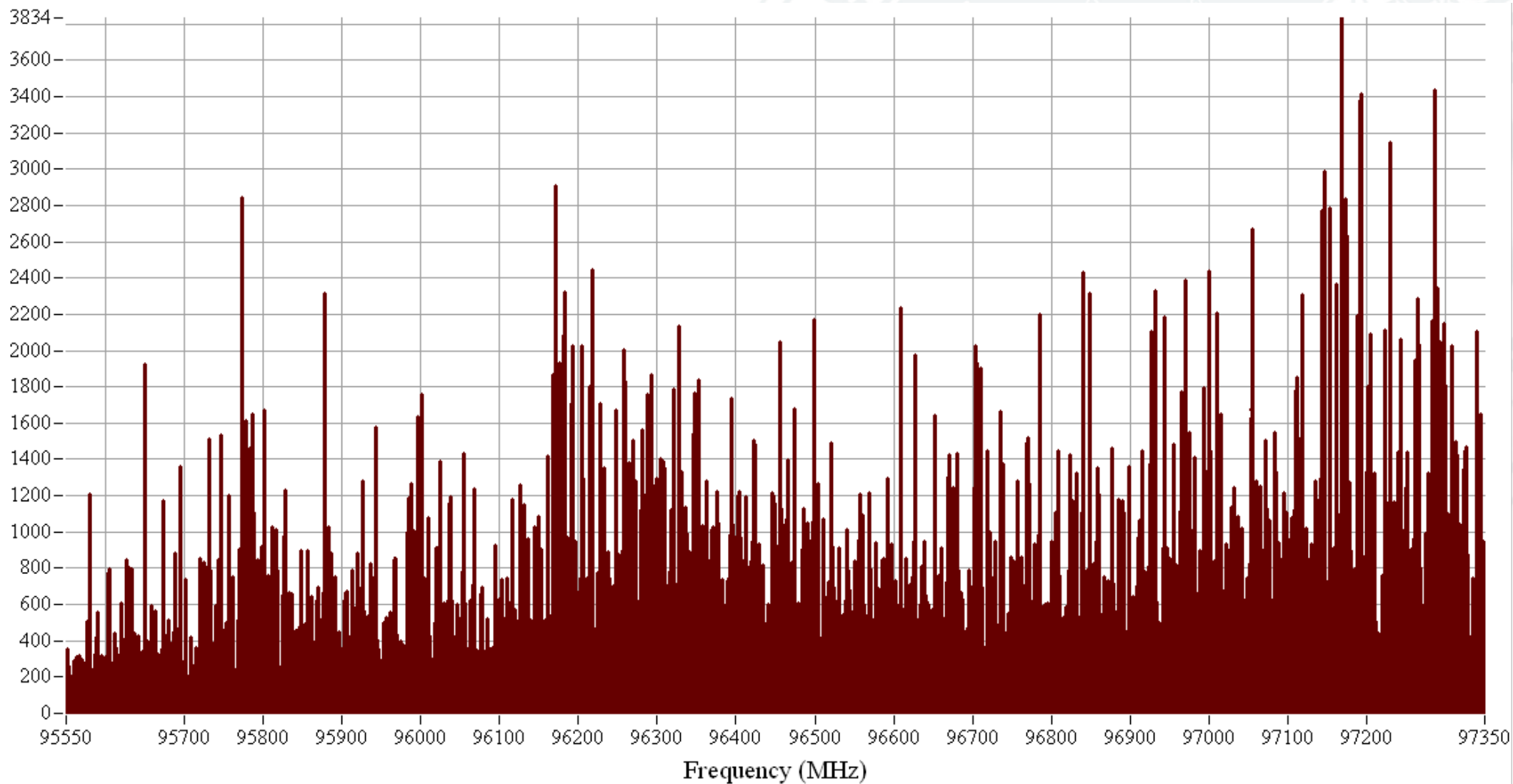
Conformers of *n*-butyl cyanide



Abundances: Crowder 1989 (IR)

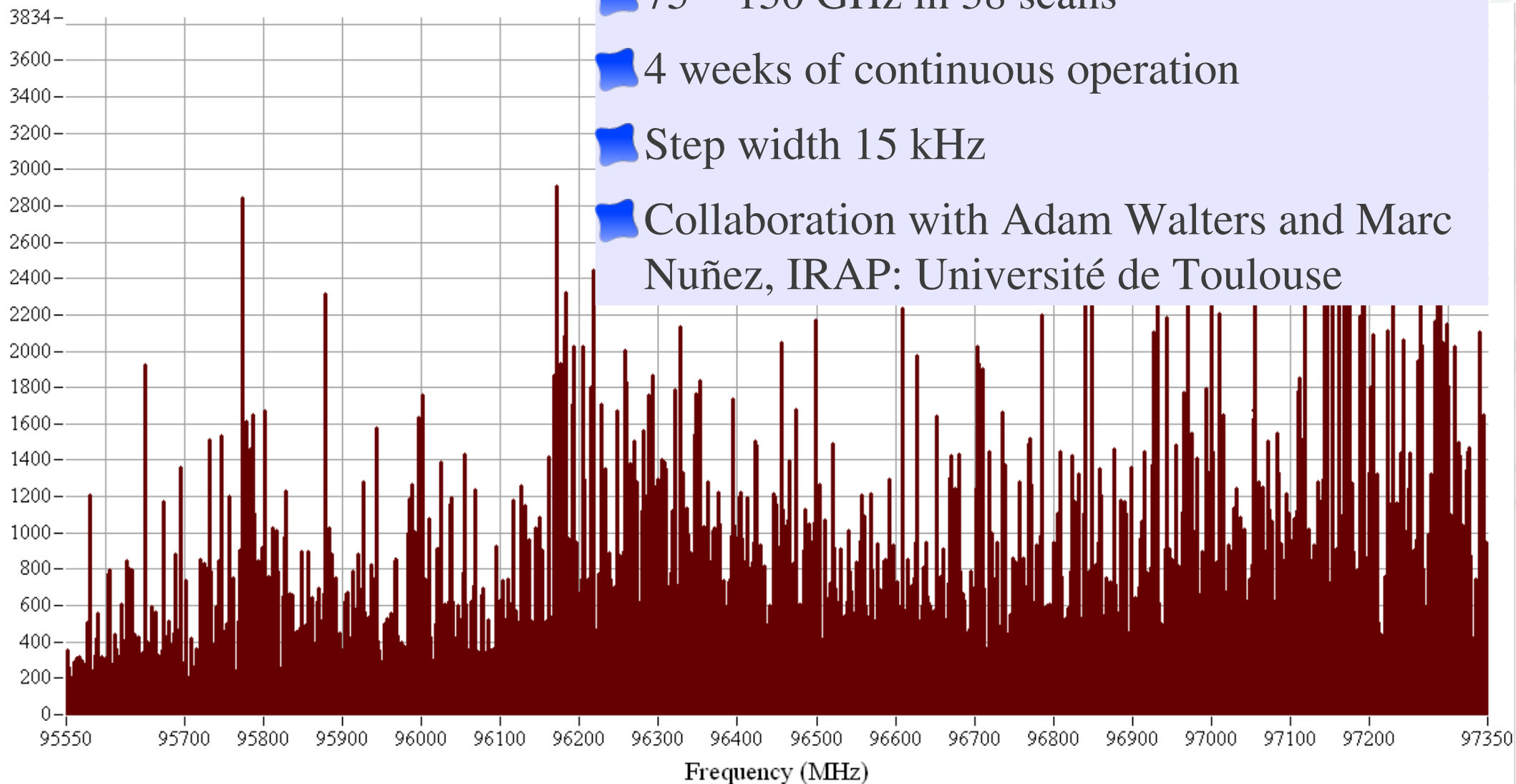


Measured MMW spectrum

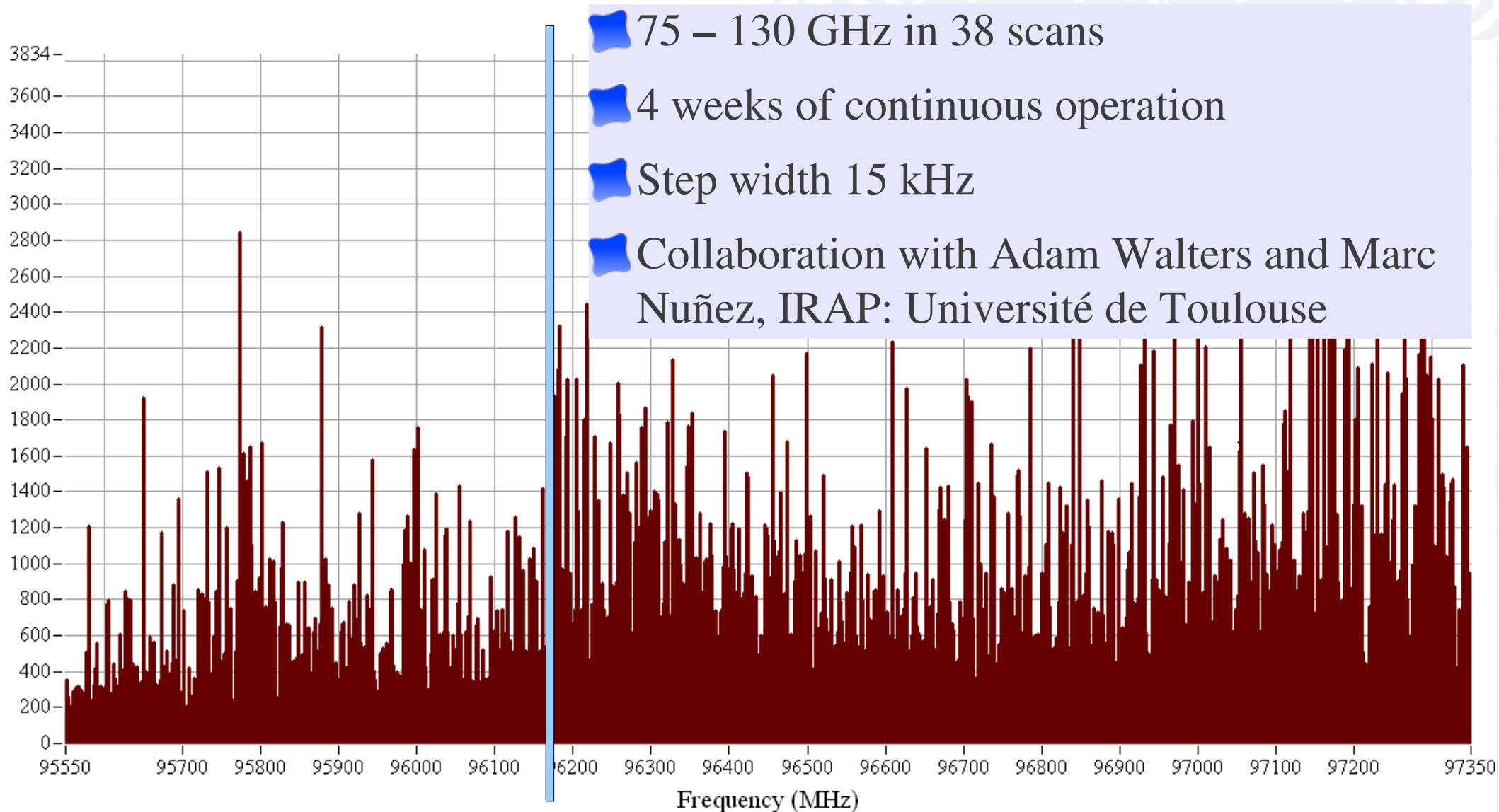


Measured MMW spectrum

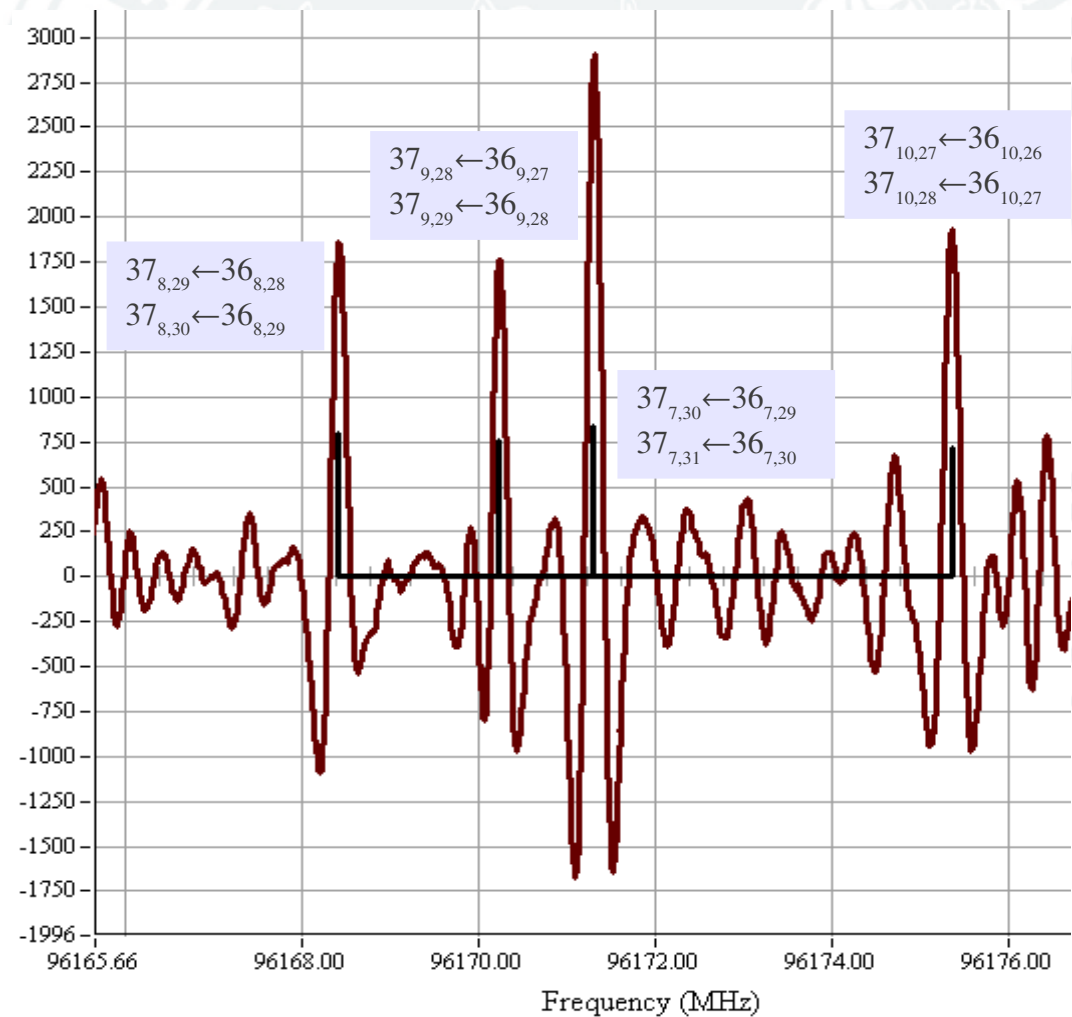
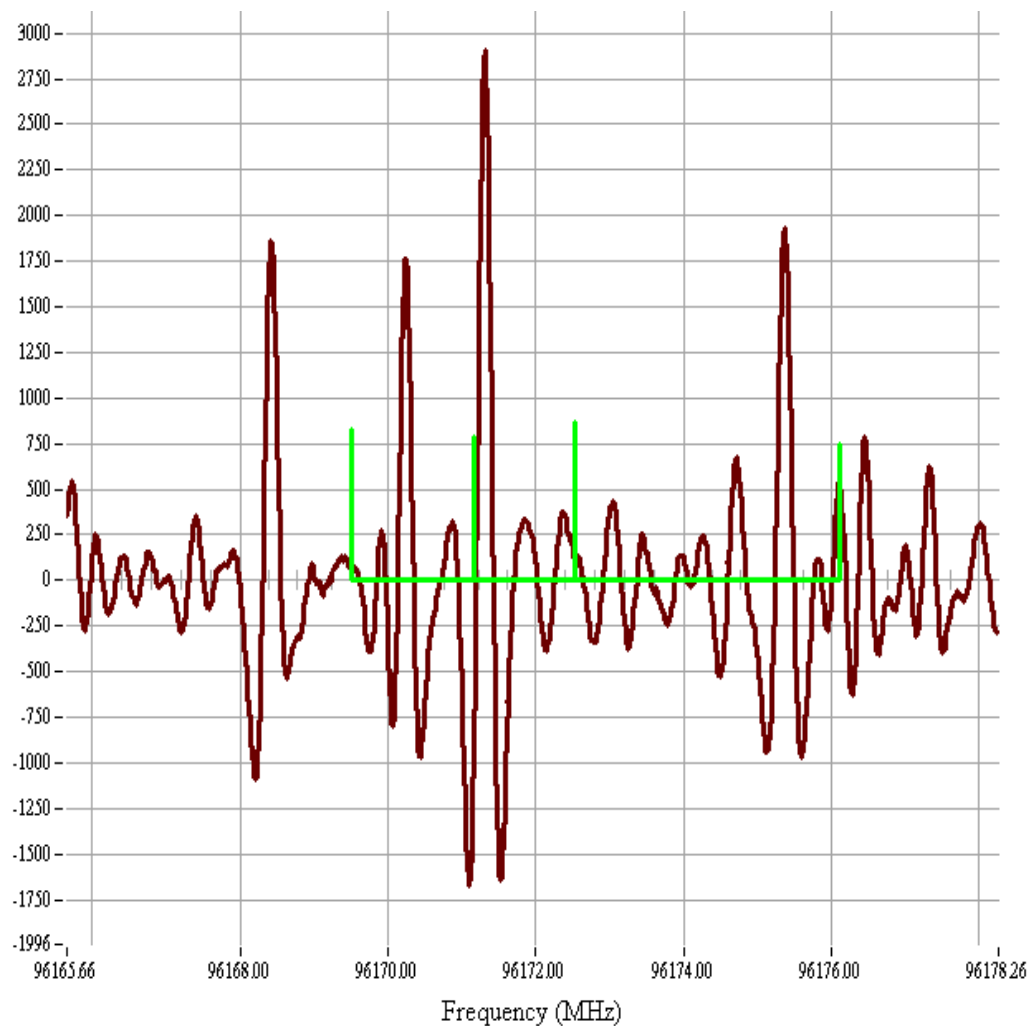
- 75 – 130 GHz in 38 scans
- 4 weeks of continuous operation
- Step width 15 kHz
- Collaboration with Adam Walters and Marc Nuñez, IRAP: Université de Toulouse



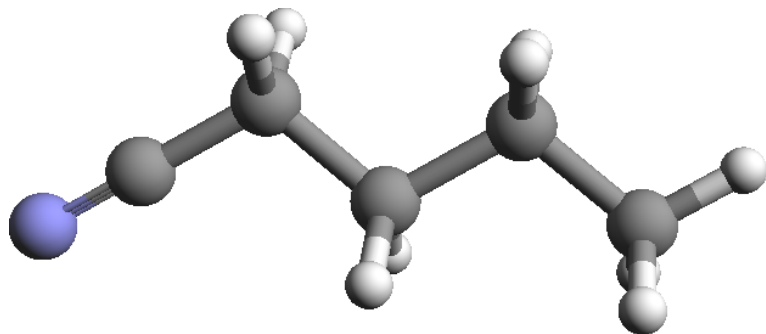
Measured MMW spectrum



Fit with SPFIT / SPCAT



Results: AA conformer



Abundance 30 %

$$\mu_a = 3.4 D$$

$$\mu_b = 1.9 D$$

$$\mu_c \sim 0.0 D$$

Constant	Bohn <i>et al.</i>	This work
A [MHz]	15028.4681(010)	15028.7074(125)
B [MHz]	1334.106100(300)	1334.106090(89)
C [MHz]	1263.857800(300)	1263.857660(95)
$-D_K$ [MHz]	—	-0.2383(124)
$-D_{JK}$ [kHz]	7.63000(3000)	7.54189(49)
$-D_J$ [kHz]	-0.148900(1100)	-0.145077(49)
d_1 [kHz]	-0.0206000(14000)	-0.0219135(144)
d_2 [Hz]	—	-0.3499(210)
H_{KJ} [Hz]	—	To be published
H_{JK} [mHz]	—	
H_J [mHz]	—	
L_{KKJ} [mHz]	—	
Lines	27	1090
Std.dev. [MHz]	0.0027	0.0206

Bohn et al. 1997:

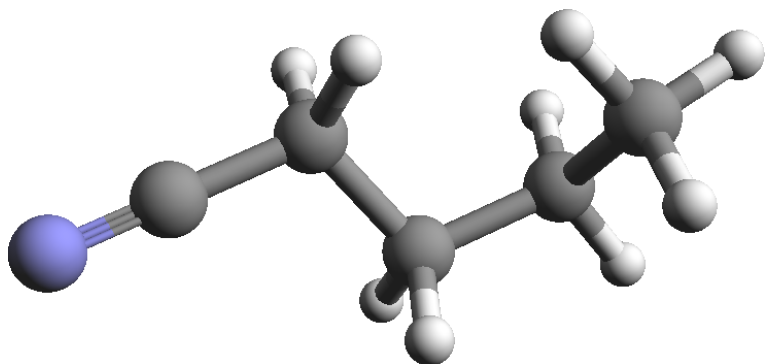
FTMW ≤ 21 GHz

^{14}N -HFS splittings

Dipole moments (calculated)



Results: AG conformer



Abundance 13 %

$$\mu_a = 3.7 D$$

$$\mu_b \sim 0.0 D$$

$$\mu_c = 1.2 D$$

Constant	Bohn <i>et al.</i>	This work
A [MHz]	11887.46590(170)	11887.56523(56)
B [MHz]	1486.185400(500)	1486.185652(156)
C [MHz]	1415.762100(500)	1415.762227(161)
$-D_K$ [MHz]	—	-0.1(0)
$-D_{JK}$ [kHz]	2.79300(600)	2.73356(53)
$-D_J$ [kHz]	-0.226000(3000)	-0.227000(72)
d_1 [kHz]	-0.0160000(30000)	-0.0157727(291)
d_2 [Hz]	—	-2.2415(183)
H_{KJ} [Hz]	—	To be published
H_{JK} [mHz]	—	
H_J [mHz]	—	
L_{KKJ} [mHz]	—	
Lines	21	947
Std.dev. [MHz]	0.0034	0.0246

Bohn et al. 1997:

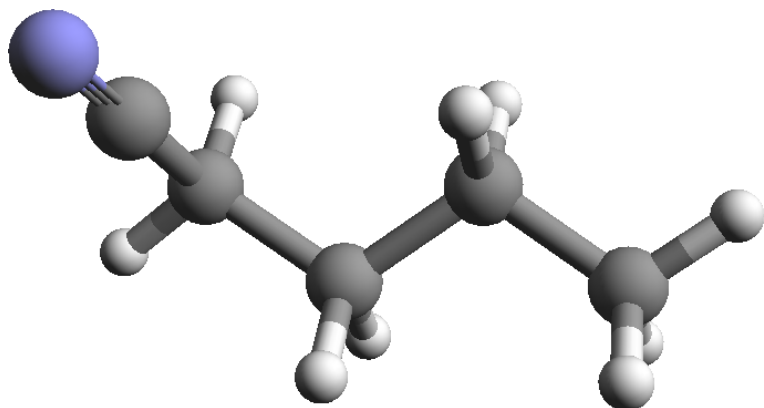
FTMW ≤ 21 GHz

^{14}N -HFS splittings

Dipole moments (calculated)



Results: GA conformer



Abundance 46 %

$$\mu_a = 3,4 D$$

$$\mu_b = 1,9 D$$

$$\mu_c \sim 0,0 D$$

Constant	Bohn <i>et al.</i>	This work
A [MHz]	7635.621000(2000)	7635.621872(284)
B [MHz]	1788.632700(300)	1788.633069(58)
C [MHz]	1554.221300(300)	1554.221330(62)
$-D_K$ [kHz]	-52.7000(3000)	-52.3424(86)
$-D_{JK}$ [kHz]	10.12000(6000)	9.89704(56)
$-D_J$ [kHz]	-0.8500000(500000)	-0.8600208(303)
d_1 [kHz]	-0.2238000(14000)	-0.2330517(57)
d_2 [Hz]	—	-8.5369(36)
H_K [Hz]	—	To be published
H_{KJ} [Hz]	—	
H_{JK} [Hz]	—	
Lines	23	1056
Std.dev. [MHz]	0.0034	0.0309

Bohn et al. 1997:

FTMW ≤ 21 GHz

^{14}N -HFS splittings

Dipole moments (calculated)



Conclusion and Outlook



Summary: Results so far

■ Spectrometer with 14-fold increased sensitivity

- ▶ $\mu_{min} \sim 2,7 \cdot 10^{-7} \text{ cm}^{-1}$

■ *n*-butyl cyanide:

- ▶ Strongly expanded data base

- ▶ Considerably higher quantum numbers, $J_{max} = 49, K_{max} = 32$

- ▶ First predictions of several lines up to 300 GHz possible
($\Delta\nu = 100 \text{ kHz} \dots 1 \text{ MHz}$; $T = 300 \text{ K}$)



Outlook

- Radio Telescope Effelsberg
 - ▶ Collaboration with Karl Menten, MPIfR Bonn
- 200 GHz measurements
- Predict spectra for the GG conformers
- Isomers
- Isotopologues
- More complex molecules



Thank you

- This work was funded by the German Research Council via grant SFB 956
- U Cologne: H.S.P. Müller, F. Lewen, and S. Schlemmer
- U Toulouse: M. Nuñez and A. Walters
- Thanks for your attention!

